# The Structure of Di- and Tri-Valent Metals*

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The structures of the di- and tri-valent metals Be to Hg and Al to Tl are considered from a fundamental point of view, based on the pseudopotential and second order perturbation theory. The most significant factors for the structure of a simple metal are the valence $z$, and the position $q_o$ of the first zero of the pseudopotential. The $q_o$ in turn can be related to atomic properties such as the radius of the ion core and the sp promotion energy. When $q_o$ falls near a set of reciprocal lattice vectors, distortions from a simple structure are likely to occur. The variation of $q_o$ through the periodic table gives a qualitative explanation of the variation of c/a ratio from Be to Cd, the occurrence of distorted structures in Hg, Ga and In, the

behavior of the InPb and InSn solid solution alloys, as well as features of the molten metals and some other elements. A few detailed calculations show the qualitative arguments are soundly based, but the pseudopotentials have to be very precisely known, which they are not at present, before good agreement with experiment can be expected.

# I. THE STRUCTURAL ENERGY

We are interested in understanding the structures of metals from a fundamental point of view. Basically the cohesive energy of a metal depends on the electronic structure of the conduction band, which we describe in terms of pseudopotentials in the way now customary.[1,2] Previous attempts to predict the observed structures of metals from first principles using such a theory have met with mixed success.[2] Recognizing the uncertainty of our present knowledge of atomic pseudopotentials $v(q)$, particularly at large wave number[3] $q$, and of the precise dependence of the exchange and correlation energies on structure, we shall here content ourselves with the qualitative explanation of well-defined trends in the structures of metals in terms of trends in the corresponding pseudopotentials. The metals considered are those with valency $\mathcal{Z} = 2$ (Be, Mg, Zn, Cd, Hg) and $\mathcal{Z} = 3$ (Al, Ga, In, Tl), and some alloys of them. We omit Ca, Sr, Ba and Sc, Y, La because the proximity of d-states has a strong effect, as may be seen for example from the $A_2$ parameter and the peculiar $v(q)$ for Ca, etc.[3] At the end (Sec. VI) we include a few brief comments on some other elements.

Since the pseudopotential is small, the total energy is expanded in a perturbation series. To first order, the conduction band is a free-electron gas with the bottom of the band given by the mean pseudopotential, and the total energy a

function of volume only, $U_1$, say. The structure dependent second order energy is[4-6]

$$U_2 = U_E + \Sigma_g W(g)[v(g)]^2 F(g) \qquad (1)$$

Here W(g) is the structural weight of a set of reciprocal lattice vectors $\underset{\sim}{g}$,

$$W(g) = \sum_{\underset{\sim}{g}} |S(\underset{\sim}{g})|^2 \qquad (2)$$

where S is the structure factor, and the sum is over all equivalent reciprocal lattice vectors $\underset{\sim}{g}$.

F contains two factors:

$$F(q) = \alpha(q) f(q), \qquad (3)$$

with f(q) the usual function from perturbation theory

$$f(q) = \sum_{k<k_F} \frac{1}{T(\underset{\sim}{k}) - T(\underset{\sim}{k}+\underset{\sim}{q})}$$

$$= \frac{\Omega k_F}{4\pi^2}\left[1 + \frac{4k_F^2 - q^2}{4qk_F}\log\left|\frac{q+2k_F}{q-2k_F}\right|\right] \qquad (4)$$

depicted in Fig. 1, where $T(\underset{\sim}{k}) = \hbar^2 k^2/2m$ and $k_F$ is the radius of the Fermi sphere. In (3) , $\alpha(q)$ is a slowly varying function of order unity which includes among other things the exchange and correlation energy: We shall for the most part ignore it. We discuss $\alpha$ and Eq. (1) further in the appendix. The quantity

$$E(q) = [v(q)]^2 \alpha(q) f(q) \qquad (5)$$

in (1) is the energy characteristic of Harrison[2,4] and we shall cast most of our discussion in terms of it. Finally $U_E$ in (1) is an Ewald term,[7] the difference between the electrostatic potential energy of the real lattice and the potential energy $-0.9\, \mathcal{Z}^2 e^2/R_a$ when the atomic polyhedron is replaced by a sphere of radius $R_a$.

We have omitted in (1):

(a) Higher order perturbation terms. These are of small order since typically[3] $v(g)/E_F \approx 0.1$, though they can lead to some observable effects.[8]

(b) Core-core interactions. These should be small since among the metals considered the ion cores are small, tightly bound, and not overlapping.

(c) The effect of the non-locality of the pseudopotential. In most metals the parameters $A_0$ and $A_1$ of the model

potential[3] do not differ greatly so that v is nearly local. Also in (1), (4) most of the contribution comes from scattering between states near the Fermi level because of the energy denominator, so that the relevant scattering matrix element $\langle k \mid v \mid k + q \rangle$ is nearly constant, which is all that is really assumed, even though v is not local.

(d) The exclusion of the valence states from the core. This is the 'orthogonality correction'[3] and leads to a small change[4,5] in the effective $\mathcal{Z}$.

Finally we make one further approximation of a somewhat different nature: We include in (1) only the first few reciprocal lattice vectors $g < 2k_F$. On the one hand f(q) decreases to zero as $q \to \infty$, and on the other there are grounds[9] for hoping that v(q) may be taken to cut off fairly quickly at large q.

All of this would be of little use were it not for the fact that the pseudopotentials v(q) of most elements are astonishingly similar,[3] passing through zero at some point $q_o$ usually less than $2k_F$ (Fig. 2). The shape of E(q) depicted in Fig. 3 is indeed typical, and its qualitative variation from element to element is contained in the two parameters $q_o$ and $2k_F$. The appropriate scale on which to measure these quantities is one in which the

reciprocal lattice vectors g, at which E(q) is to be evaluated, are fixed. We use as unit $2\pi/A_o$ where $A_o$ is the lattice constant of a face-centered cubic (f c c ) structure with the same atomic volume. $2k_F$ is then a function only of valence $z$ . The variation of $q_o$ will be considered in the next section.

How do we expect the structure to depend on these parameters? Firstly it is clear that a set of reciprocal lattice vectors of magnitude $g \gtrsim q_o$ will contribute little to the binding energy. In choosing between two simple structures, e.g., body-centered cubic (b c c ) and hexagonal close packed (h c p ), the effect of $q_o$ is to favor the structure which has a distribution of structural weight avoiding it. Bigger band gaps simply give bigger binding energy. Furthermore, a structure having a set of reciprocal lattice vectors falling near $q_o$ may lower its total energy by splitting them into two or more sets by an appropriate distortion of the lattice. This effect, which is due to the convexity of E(q) near $q_o$ (Fig. 3), has a converse in any region where there is a strong concave (i.e., upward) curvature of E(q), as is the case for q just less than $2k_F$ in many metals.

We should note, however, that the effect of the Ewald term $U_E$ in (1) is to favor a structure of high symmetry such as f c c , b c c and h c p. The Ewald energy of these is small, quite negligible in fact,[7] but it appears to increase rapidly with any distortion of them.

The lowering of the energy $U_2$ by the repulsion of a reciprocal lattice vector g away from $q_o$ applies whether the change in g is due to a change of volume or of structure. However, an electron gas is rather incompressible because of the Fermi energy, and $U_2$ being second order in v is small. The volume changes induced by $q_o$ are consequently very small, and we shall in what follows, consider only the change in $U_2$ with structure at constant volume.

The behavior of f(q) in the region of the singularity at $2k_F$ results in a sharp increase in the gradient of E(q) there. In the simple second order theory, the gradient in fact becomes infinite. Other things being equal, i.e., v(q) constant, it pays to have a reciprocal lattice vector below $2k_F$ rather than above. This is the well-known effect discussed by Mott and Jones[10] in terms of the formation of Jones zones near the Fermi sphere.

In the case of distorted structures, this effect can determine the magnitude of the distortion. Suppose a set of reciprocal lattice vectors g increases with distortion. When $g = 2k_F$, the infinite gradient makes it energetically unfavorable for the distortion to increase. In practice, of course, the singularity is somewhat smoothed out. Also v(q) may be increasing sufficiently rapidly that E(q) is still decreasing beyond $q = 2k_F$. Nevertheless a fairly sharp increase (in the algebraic sense) of dE/dq near $2k_F$ will remain, and can suffice to limit the distortion.

## II. VARIATION OF $q_o$

Since we ultimately wish to understand the structures of solids in terms of the basic properties of atoms, it is important to relate the variation of $q_o$ among the elements to atomic features.

The cancellation theorem[11,12,13] suggests as an approximate picture (in real space) of the pseudopotential of a bare ion

$$V_{ps} = \bar{V}, \quad r < R_c, \qquad (6)$$
$$= -\mathcal{Z}/r, \quad r > R_c,$$

where all the real potential is cancelled off to $\bar{V}$ inside the core radius $R_c$. $\bar{V}$ is the mean screened pseudopotential in the metal, approximately proportional to $\mathcal{Z}$. Thus, $V_{ps}/\mathcal{Z}$ is a function of $r/R_c$ only, and $q_o$ proportional to $1/R_c$. The screening by the electron gas only affects the magnitude of $v(q)$ through the screening factor $\epsilon(q)$ without altering $q_o$. It is easy to verify this simple model gives $q_o$ in approximately the observed place: ignoring $\bar{V}$ in (6) gives $v(q) \propto q^{-2} \cos(qR_c)$ with $q_o R_c = \frac{1}{2}\pi$ which is somewhat too far out, and the effect of $\bar{V}$ is to bring $q_o$ in a bit. Anyway $q_o$ is proportional to $R_a/R_c$ in units of $2\pi/A_o$, where $R_a$ is the atomic radius.

Empirically $R_a/R_c$ increases with $\gamma$, as can be understood in terms of pseudopotentials.[14] Thus, $q_o$ increases with $\gamma$, as can be seen in Fig. 4 by comparing pairs of elements from the same row of the periodic table or the means of the two groups $\gamma = 2$ and $\gamma = 3$.

Within a group of constant $\gamma$, there is some decrease in $R_a/R_c$ with increasing atomic number Z[14] which would tend to decrease $q_o$. However, this effect is outweighed by another. The energy difference $\Delta_{sp}$ between the s and p states in the atom increases (relative to the energy levels themselves) with increasing Z. It is the well-known fact that the s shell in Hg, Tl , Pb is relatively rather tightly bound, and can also be partly described in terms of pseudopotentials[14] but not within the simple model (6). A large $\Delta_{sp}$ tends to make v(q) more negative, i.e., to give the s-like state below the p-like one at a band gap at constant g.[15] Thus, $q_o$ increases with atomic number Z in each group of constant valence $\gamma$, as can also be seen in Fig. 4.

## III. THE DIVALENT METALS

Fig. 4 shows the structural weights W(g) of the f c c, b c c and h c p. (ideal c/a) structures, relative to $q_o$ and $2k_F$ for the divalent metals. The $q_o$ are values calculated from the Model Potential,[3] which gives good agreement with experiment,[3,16] for v(q) in the region of $q_o$. It is immediately clear that the f c c structure is unfavorable because its structural weight is split between two g's in a region where E(q) is concave. For Zn, Cd, h c p is favored over b c c since the main structural weight lies further from $q_o$. The balance is more even for Be and Mg where $q_o$ is considerably smaller: We shall merely accept that h c p is the stable form and turn to the deviation of the c/a ratio from the ideal. Hg will be treated as a special case in Section IV.

For the h c p structure, the Ewald energy is a minimum for the ideal (close packing) c/a ratio, but there is no group-theoretical argument (as there is for cubic symmetry) that the band structure energy shall be stationary at this c/a ratio. Thus there is a linear term in the relation of band structure energy to distortion from ideal c/a, and c/a will deviate somewhat from ideal in all cases.

The magnitudes of the reciprocal lattice vectors vary with distortion as follows:

$$g_1 = g(1\bar{1}0,0) = 1.633\ (1 + \gamma) \tag{5}$$

$$g_2 = g(000,2) = 1.732\ (1 - 2\gamma) \tag{6}$$

$$g_3 = g(1\bar{1}0,1) = 1.848\ (1 + 0.341\gamma) \tag{7}$$

$$\text{where } 1 + \gamma = \left[\frac{c/a}{c/a \text{ ideal}}\right]^{1/3}. \tag{8}$$

Each g tends to produce a change in c/a which would move it to lower E(g). For example in Zn and Cd, $g_3$ which has the largest structural weight lies in the region just to the right of $q_o$ where $E'(q) = dE/dq$ is negative. Since $g_3$ increases with c/a, it tends to give c/a greater than ideal. Using the structural weights of Fig. 4, we may write down the combined effect of $g_1$, $g_2$, $g_3$. The term in the band structure which is linear in the distortion is

$$[2.45E'(1.633) - 6.93E'(1.732) + 5.67E'(1.848)] \tag{9}$$

If the coefficient in square brackets is negative, it lowers the energy to have $\gamma$ positive, i.e., c/a greater than ideal; and vice versa. If we replace the first two reciprocal lattice

vectors, which are close together, by their mean, (9) simplifies to

$$[-4.48E'(1.688) + 5.67E'(1.848)] \qquad (10)$$

This quantity may be thought of as roughly proportional to the second derivative of E(q) at $q \approx 1.75$; it is then clear that it will decrease steadily from Be for which it will be small, the $q_o$ being at 1.39, to Cd in which it will be large and negative since the zero is at 1.70 so the reciprocal lattice vectors fall in the region of large convex curvature. This predicts a c/a ratio which increases with $q_o$ from a value close to ideal, in agreement with the observed ratios Be(1.59), Mg(1.62), Zn(1.86), Cd(1.89).

For a given element, $q_o$ can be decreased relative to the reciprocal lattice vectors by increase of pressure, and an overall increase of c/a with $q_o$ is observed,[17] though it is not monotonic.

The replacement of $g_1$ and $g_2$ by their mean neglects the effect of their motion relative to the mean. $g_1$ and $g_2$ cross over at c/a = 1.73. The effect of the convex curvature of E(q), which pushes them apart is thus to reduce c/a when it is less than 1.73 and increase it when greater. Since the curvature in this region is much greater in Zn and Cd than in Be and Mg, this is probably a significant contribution to the very large deviation of c/a from ideal for the former.

In the MgCd alloys[18] and in Cd under pressure, the variation of c/a with composition and pressure is most rapid at c/a = 1.73, which presumably is again related to the crossing of $g_1$ and $g_2$. A simple theory gives just a uniform expansion of the c/a scale about 1.73, proportional to $E''(q)$ at $q \approx 1.7$, and we conclude the effect is more complicated.

## IV. MERCURY

In Hg the main structural weight of all three structures falls close to $q_o$, so that there will be little binding in any structure. The same applies to the liquid where the main peak in a(q), the expectation value of $|S(q)|^2$, also falls nearly on $q_o$. The difference in energy $\Delta U$ between liquid and solid will also be small, resulting in a low melting temperature

$$T_m = {}^{\Delta U}/_{\Delta S} \qquad (11)$$

where $\Delta S$ is fixed by the geometrical entropy of disorder.[19]

Returning to the solid structures, we see from Fig. 4 that b c c is clearly unfavorable, since W(g) falls practically on $q_o$. The f c c structure appears favored over the h c p structure since it has some structural weight at g = 2.0, well away from $q_o$. The concentration of structural weight near $q_o$ in all three structures accounts for the preference of Hg for more complex structures whose structural weight avoids it. Two structures are found, both of which are describable as distortions of f c c, and indeed are the two types of shearing distortion of f c c which we would expect on grounds of symmetry. They are the rhombohedral distortion[20] ($\alpha$-Hg), which stretches or compresses the cubic cell along a body diagonal, splitting the {111} set of reciprocal lattice

vectors, and the tetragonal distortion[21] ($\beta$ - Hg) which stretches or compresses it along a cube axis, splitting the $\{200\}$ set of reciprocal lattice vectors. The Ewald term opposes both distortions, but not equally. The rhombohedral shear is opposed much more strongly as can be seen from the Ewald contribution C(E) to the corresponding elastic constants[22]:

$$\frac{C_{44}(E)}{\frac{1}{2}[C_{11}(E)-C_{12}(E)]} = 8.95. \qquad (12)$$

This is presumably why both structures are found, despite the fact that the rhombohedral distortion, since it splits the set of reciprocal lattice vectors close to $q_o$, appears much more favorable from the point of view of lowering the band structure energy. Indeed, since the tetragonal distortion splits the $\{200\}$ set which does not lie in a region of convex curvature of E(q), and shifts the $\{111\}$ set, which lies close to $q_o$ where the derivative of E(q) is small, the f c c structure may well be stable against a small tetragonal distortion. This does not, however, imply that the very large observed distortion ($c/a = \frac{1}{2}$) is unfavorable. Note in particular, that the contribution of the $\{111\}$ reciprocal lattice vectors to the cohesive energy will increase roughly as the fourth power of distortion because they are near $q_o$.

Both types of distortion have magnitudes which are in keeping with the discussion in Sec. I, i.e., limited by a set of reciprocal lattice vectors reaching $2k_F$ from below. Two of the $\{111\}$ vectors in $\alpha$-Hg are at 1.03 $(2k_F)$, while in $\beta$-Hg the whole set $\{111\}$ is at 1.02 $(2k_F)$.

The main point which we wish to emphasize here is that these distortions stem from $v(g)$ being small, i.e., $g$ being near $q_o$. How far may they be viewed as some tendency to form covalent bonds of particular lengths and angles? Certainly not in the sense of the diamond type semiconductors, where the covalency is a manifestation of $v(g)$ being large.[9] However, the form of $v(q)$, in particular the position of $q_o$, is presumably related to bond distances $d = 2\pi/q$ in molecules. In the solid the mean near-neighbor distance is more or less fixed by the atomic volume which is determined largely by the energy of the free electron gas as a function of volume. In mercury it happens accidentally to fall near $d_o = 2\pi/q_o$. In a molecule the electron gas is not confined in the same way, and (supposing covalent binding) the bond length $d$ is probably more directly determined by $v(q)$. We expect $d < d_o$, corresponding to $q > q_o$ and $v(q)$ positive. This denotes heaping up of charge between the atoms, i.e., an sp bond. If this is a correct picture, then the distortion in the solid to give some neighbor distances $d < d_o$ is not unrelated to covalent bond lengths in molecules. There is some evidence for this. Ideally we would like to compare with bond lengths in diatomic molecules in the metal vapors. These data are not available. Values for

the oxides are given in Table I. The first line gives metal-oxygen distances[23] in the oxide, the mean for ZnO, ZnS and NaCl structures being given where the oxide exists in more than one form. $R_{ox}$ is a metal atom radius in the oxide obtained by subtracting 0.83 from the M-O distances. Since we are concerned with the trend, it is arbitrary what number we subtract. We have chosen it to give $R_{ox}=R_m$ for Mg, where $R_m$ is the atomic radius in the metal in the sense that $(4\pi/3)R_m^3$ is the volume per atom. We note that $R_{ox}$ for Hg is abnormally smaller than $R_m$ as expected from the small $2\pi/q_o$, and it is probably legitimate to interpret the distortion of the Hg structure as an attempt to obtain some nearest neighbor distances less than those in a regular fcc structure at the same atomic volume. We emphasize that relating the oxide spacings to pseudopotentials in this extremely crude way is only intended to make a qualitative connection between metallic structure and chemical properties, not as a useful discussion of the oxides themselves. Nor does our connection between $q_o$ and bond lengths have anything new in content, because $q_o$ is determined by the same factors normally considered for chemical properties as we have observed in Sec. II, namely ionic radius, binding of the lowest s-state of the atom and the promotion energy $\Delta_{sp}$.

## V. TRIVALENT METALS

The zero of the Al pseudopotential falls close to those of Cd and Zn, yet Al has the f c c structure, presumably because the $\{200\}$ set of reciprocal lattice vectors falls below $2k_F$ for $\mathcal{Z} = 3$ (Fig. 4), and its contribution to the cohesive energy of the f c c structure is correspondingly increased.

Since Cd and Zn show considerable distortion from the ideal h c p structure, and Hg from the f c c, we may also ask why Al is undistorted f c c. Table II shows the observed shear elastic constants of Al, together with the contribution of the Ewald term and the difference, which is the band structure contribution. The latter is large and negative for $C_{44}$ (rhombohedral distortion), because this corresponds to a splitting of the $\{111\}$ set, lying close to $q_o$, in the region of strong curvature of E(q). The band structure contribution to $\frac{1}{2}(C_{11}-C_{12})$, corresponding to tetragonal distortion is small and positive since g(200) lies outside this region. Thus the position of $q_o$ is responsible for the fact that the band structure contribution to the elastic constants has a large anisotropy, opposite to that of the Ewald term, giving nearly isotropic total elastic constants.[2,24] The fact that $C_{44}$ (band structure) does not outweigh $C_{44}$ (Ewald), giving a total negative $C_{44}$ and a spontaneous rhombohedral distortion as in the case of Hg, may be regarded as a consequence of the smaller atomic volume

and larger valence of Al, both of which increase the relative size of the Ewald term.

Ga, In, Tl have $q_o$ lying successively to the right of Al. If $q_o$ lies in the region 1.6-1.7 as it does for Ga and indium, the simple structure with lowest energy is clearly f c c. However, even for f c c both g(111) and g(200) will lie near the peak of E(q), and the band structure energy will strongly favor more complicated structures, which have a distribution of structural weight which better avoids $q_o$. Though the effect is greater for Ga, we will consider first the simpler case of indium. The indium structure is a small tetragonal distortion[23] of f c c, with c/a = 1.08. The $q_o$ lies midway between g(111) and g(200), making the curvature strong at each, especially g(111), but the tetragonal rather than rhombohedral distortion occurs, because of the preference of the Ewald term (see Eq. 12). We have calculated $\frac{1}{2}(C_{11}-C_{12})$ for the f c c structure, corresponding to tetragonal distortion, as $q_o$ varies from 1.66 for Al to 1.86 for indium. We take the pseudopotential to be (in Ry):

$$v(q) = 0.5\ (D^2 - .83^2)\ \exp\ (-D^2) \qquad (13)$$

where $D = \alpha q/2k_F$. This roughly fits the Model Potential[3] for indium when $\alpha = 1$ and Al for $\alpha = 1.12$, variation of $\alpha$ corresponding to stretching the curve along the q-axis. The result for the band structure contribution to $\frac{1}{2}(C_{11}-C_{12})$ is shown in Fig. 5. When $q_o$ falls in the region appropriate to Al,

$\frac{1}{2}(C_{11}-C_{12})$ is small and positive, but decreases sharply as $q_o$ moves to the right, corresponding to the extreme sensitivity of the calculated spectrum of Al to the assumed value of $q_o$, noticed by Vosko et al.[25] The value for $\alpha = 1$, i.e., indium, more than cancels the Ewald contribution.

More complete calculations for indium are shown in Table III. The first column gives the observed values, and the others the calculated values using respectively, (i) the calculated pseudopotential of Animalu and Heine[3](AH) taking all higher reciprocal lattice vectors into account, and (ii) the pseudopotential (Fig. 2) fitted by Cohen and Bergstresser[26](CB) to the optical spectrum of InSb. The AH potential predicts too great an instability apparently due to its having too large a gradient at g(200). It is interesting to note that the v(q) fitted empirically for InSb gives much better answers. In any case it is clear that the qualitative remarks in Sec. I about the origin of distortions make quantitative sense. But because of the cancellation between band structure and Ewald terms, the pseudopotential has to be known very precisely before good agreement with experiment can be expected.

While indium shows only a slight tetragonal distortion from f.c.c., the two known forms of Ga are both complicated orthorhombic structures,[27,28] Ga I and II. The crucial difference is not the position of $q_o$, which is almost identical (Fig. 4), but the slope of v(q), which, from calculated,[3] and

empirically fitted pseudopotentials[26] is found to be about 1.2 times greater for Ga. Since $v(q)$ appears squared in $E(q)$, the negative band structure contribution to the elastic constant $\frac{1}{2}(C_{11}-C_{12})$ is about 1.4 times larger. Whereas in indium it scarcely outweighs the resistance to distortion of the Ewald term, in Ga there will be a much greater tendency to distortion and the structure will be more radically modified. If Ga had the same tetragonal form as indium, limited by a set of reciprocal lattice vectors reaching $2k_F$ as in Hg (Sec. IV), the c/a ratio would be about 0.85 or 1.3. The GaI structure[27] may be obtained from the c/a = 0.85 face centered tetragonal structure by a rearrangement consisting mainly of the sliding of consecutive atomic layers perpendicular to the c-axis, giving an orthorhombic structure with

$$a \approx b, \quad c/a = 2 \times 0.85 = 1.7. \tag{14}$$

The GaII structure[28] also has a set of reciprocal lattice vectors at $2k_F$.

For Tl, consideration of the position $q_o$ in Fig. 4 does not suggest clear preference for any of the simple structures, which is in keeping with experiment, since all three are observed,[29] h c p being the low temperature, low pressure form. The h c p structure has near ideal c/a ratio, since $E(q)$ does not have strong curvature around the reciprocal lattice vectors (see Sec. III). Comparison of the pseudopotentials of indium

and Tl would lead us to expect f'c c' Tl to have slight instability with respect to tetragonal distortion, as does indium. In fact it is just stable. The elastic constant $\frac{1}{2}(C_{11}-C_{12})$, extrapolated from alloy data,[30] is 0.32 dynes/cm$^{-2}$.

## VI. FURTHER APPLICATIONS

We will include in this section some related comments on alloys, higher valency elements and liquid metals.

We have seen in Sec. V that as $q_o$ shifts from indium to Tl, quite a large shift (Fig. 4), the elastic constant $\frac{1}{2}(C_{11}-C_{12})$ changes from -0.1 for the hypothetical f c c structure of indium to +0.3 for f c c Tl (both values being extrapolated estimates[30,31]). The change is so slight because of opposing changes from the $\{111\}$ and $\{200\}$ reciprocal lattice vectors. It is a smooth variation and the distortion of InTl alloys tends to zero at about 23% Tl beyond which the alloys are f c c. Quite a new phenomenon occurs when Sn or Pb is dissolved in indium.[32] At about 13% solute there is a phase change, the c/a ratio switching from greater than unity to less than unity. The effect must be due to electron per atom concentration e/a, because Sn and Pb have appreciably different $q_o$ and the InTl alloys show that change in $q_o$ has a minor effect. The magnitude of the distortion may be characterized by the parameter $\gamma$ where

$$1 + \gamma = (c/a)^{1/3} \qquad (15)$$

and we may expand the total energy in powers of $\gamma$, the $\gamma^2$ term giving the (negative) elastic constant. The sign of the distortion is determined by the third order term, $D\gamma^3$ say. We

find that the Ewald term gives a positive contribution to D, i.e., favors c/a < 1, whereas the band structure contribution to D is negative favoring c/a > 1. The g(200) part of the latter is

$$-\frac{4}{3}E' - 2E'' - \frac{1}{3}E''' , \qquad (16)$$

where E', E'', E''' are the derivatives of E(q) evaluated at g(200) for the undistorted f c c structure. In the simple second order theory (Eq. 5), all derivatives tend to $+\infty$ at $q = 2k_F$ because of the singularity of f(q) there, and g(200) is only 11°/₀less than $2k_F$. Too much stress must not be put on the singularity itself because it is only a logarithmic one and is, in any case, smoothed out by higher order perturbation corrections. Nevertheless, the general shape of what corresponds to the f function is not too different, increasing to a large gradient just beyond g(200). It is, therefore, to be expected that (Eq. 16) is strongly negative, outweighing the positive Ewald term to give c/a > 1 for pure indium. However, as we increase e/a by adding Sn or Pb, $2k_F$ moves further away from g(200), and the derivatives of E(q) at g(200) decrease. The singularity is also further smoothed out by the electron scattering, although it is not clear how important this factor is. While (Eq. 16) becomes less strongly negative with increasing e/a, the positive Ewald term must be increasing due to the increase in the mean ionic change. Thus beyond a certain concentration, the band structure term no longer outweighs the Ewald term and we have a change to c/a < 1.

For the tetravalent elements we would expect an increasing tendency to form distorted structures with decreasing atomic number, the exact reverse of the situation for divalent metals. Here $q_o$ lies to the right of the main concentration of structural weight,[3,26,33] furthest for Pb, closer to the main reciprocal lattice vectors in Sn, Ge, Si. However the situation is complicated by the existence of covalent bonding[9,34] which is an effect arising from higher order perturbation terms, giving rise to the diamond structure for Si, Ge and grey Sn. Under pressure Si and Ge are found to undergo a transition[35] to the tetragonally distorted metallic structure of white Sn. Thus, under pressure, which suppresses formation of the open covalently bonded structures, these elements indeed conform to our point of view, since Pb, with $q_o$ farthest to the right, is a f c c metal. At very high pressures, Pb undergoes a transition to an unknown structure.[36] The linear compression of the f c c phase at that pressure is about 8°/₀, and we note that this increases all reciprocal lattice vectors and $2k_F$ by about the same amount relative to $q_o$, which remains fixed on an absolute scale. Thus the decrease in volume effectively moves $q_o$ to the left to about[3,33] 2.00 in our units of $2\pi/A_o$, which is near where $q_o$ lies[3] for Sn ($q_o = 2.01\ ^{2\pi}/A_o$). Thus we expect the new phase of Pb to be a distorted one.

The group V semi-metals As, Sb, Bi have a structure which is obtained from simple cubic by a rhombohedral distortion and an internal displacement.[37] Although in detail the factors

determining the structure are very complicated,[38] it is interesting to note that the g(111) set of reciprocal lattice vectors, which is split by the rhombohedral distortion, is close to $q_o$ for all three elements, and that the distortion is greatest in As, which has the strongest pseudopotential.[3]

In liquids the analog of W(g) is the structure function a(q) measured by X-ray or neutron diffraction, which has its main peak in the range of q where the simple structures have their first reciprocal lattice vectors (Fig. 4). To a first approximation a(q) is the same for all metals, but we might expect some deviations in the sense of the main weight of a(q) avoiding $q_o$. Indeed for Ga there is a splitting of the main peak, or rather a shoulder on it,[39] in such a way that a(q) is reduced around 2.8 $A^{o-1}$ which is ~~approximately~~ where $q_o$ lies (interpolated in the results of Reference 26). The effect is particularly marked for Ga because of the strength of the pseudopotential and low temperature at which observations are possible. Indium should have a similar feature in a(q), but less marked. This has not been clearly observed to date.[40] The effect is, however, clearly seen in Hg[41] and Sn[42], again explicable by a diminution of a(q) in the vicinity of $q_o$. We note incidentally that the minimum in the melting point[43] of the $\mathcal{Z} = 3$ metals correlates with the proximity of $q_o$ to the main reciprocal lattice vectors (Fig. 4) as in the $\mathcal{Z} = 2$ metals.

In Zn and Cd, $q_o$ apparently falls nearer the center of the peak in a(q) than in Hg where it lies just on the high q side.[41,44] Thus Zn and Cd have lower resistivities[45] than Hg, but higher melting points because the effect decreases the binding of the liquid.

## APPENDIX

In a one-electron formulation, the $\alpha(g)$ of (3) is just $\epsilon_2(g)$, the screening factor in v(q). It is defined by

$$v(q) = v_q^{\,b}/\epsilon_2(q), \tag{A-1}$$

where $v_q^{\,b}$ is the pseudopotential of a bare ion. In this form (1) is contained in the results of Harrison,[2,4] and Pick and Sarma,[5] but may be derived more directly as follows. Consider a single $\underset{\sim}{g}$ and ignore $S(\underset{\sim}{g})$ which we suppose equal to unity. The second order contribution to the one-electron energy of the state $\underset{\sim}{k}$ is

$$\frac{[v(g)]^2}{T(\underset{\sim}{k}) - T(\underset{\sim}{k}+\underset{\sim}{g})} \tag{A-2}$$

This has to be summed over all occupied states inside the Fermi surface, which to second order may be taken as the unperturbed Fermi sphere. We obtain, using (4),

$$[v(g)]^2 \, f(g) \tag{A-3}$$

as the major contribution to $U_2$. However, this counts the electron-electron electrostatic energy twice and we have to subtract it once.[46] It is

$$\frac{1}{2} \, \rho_{\underset{\sim}{g}} \, v_{\underset{\sim}{g}}^{\,sc}, \tag{A-4}$$

where $v_g^{\,sc}$ is the screening potential of the electron gas and $\rho_{\underset{\sim}{g}}$

the corresponding component of the electron charge density. From (A-1) we have

$$v_{\underset{\sim}{g}}^{sc} = v(g) - v_g^{b} = v(g)\,[1 - \epsilon_2(g)] \qquad \text{(A-5)}$$

$\rho_{\underset{\sim}{g}}$ comes from the perturbed wave functions

$$\psi_{\underset{\sim}{k}} = \exp(i\underset{\sim}{k}\cdot\underset{\sim}{r}) + \frac{v(g)}{T(\underset{\sim}{k}) - T(\underset{\sim}{k}+\underset{\sim}{g})} \exp i(\underset{\sim}{k}+\underset{\sim}{g})\cdot\underset{\sim}{r}\,. \qquad \text{(A-6)}$$

$\psi_{\underset{\sim}{k}}^{*}\psi_{\underset{\sim}{k}}$ makes a contribution

$$2v(g)\,[T(\underset{\sim}{k}) - T(\underset{\sim}{k}+\underset{\sim}{g})]^{-1} \qquad \text{(A-7)}$$

to $\rho_{\underset{\sim}{g}}$, and the total $\rho_{\underset{\sim}{g}}$ is

$$\rho_{\underset{\sim}{g}} = 2\,v(g)\;\; f(g). \qquad \text{(A-8)}$$

Substituting (A-5 and (A-8) into (A-4) and subtracting it from (A-3) gives

$$U_2 \;=\; [v(g)]^2\,\epsilon_2(g)\;\; f(g) \qquad \text{(A-9)}$$

apart from the Ewald term $U_E$ in (1) which does not depend on the pseudopotential.

The above calculation includes exchange and correlation only in so far as all vertex corrections are included in the screening factor $\epsilon_2(q)$ which is the 'proton-electron dielectric constant' in the sense of reference 47. It does not include the change in the exchange and correlation energy of the electron gas due to the density modulation $\rho_g$. The correct result

including this is[48]

$$\frac{\Omega g^2}{8\pi e^2} [v_g^b]^2 \left[\frac{1}{\epsilon_1(g)} - 1\right], \qquad \text{(A-10)}$$

where $\epsilon_1$ is the true 'proton-proton' dielectric constant.[47] Comparison with (1), (3) and (A-1) gives

$$\alpha(g) = \frac{g^2\Omega}{8\pi e^2} \frac{(1-\epsilon_1)\epsilon_2^2}{f\epsilon_1} . \qquad \text{(A-11)}$$

$(1-\epsilon_1)$ and f have a similar singularity at $2k_F$ so that $\alpha$ is a smooth function of g. The result (A-10) is just the operational definition of $\epsilon_1$. If we "turn on" the bare pseudopotential $v_g^b$, the change in energy is[49]

$$\frac{1}{2} \rho_{\underset{\sim}{g}}^b v_{\underset{\sim}{g}}^b / \epsilon_1(g) \qquad \text{(A-12)}$$

as in charging up an electrostatic system. The $\rho_{\underset{\sim}{g}}^b$ is proportional to $v_{\underset{\sim}{g}}^b$ by Poisson's equation and (A-12) becomes

$$\frac{1}{2} (g^2\Omega/4\pi e^2) [v_{\underset{\sim}{g}}^b]^2/\epsilon_1(g) . \qquad \text{(A-13)}$$

We can now divide this up into the direct interaction of the bare pseudopotentials

$$\frac{1}{2} (g^2\Omega/4\pi e^2) [v_{\underset{\sim}{g}}^b]^2 \qquad \text{(A-14)}$$

which is included in $U_E$, and the remainder (A-10) which is the interaction via the screening electrons.

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49 We are indebted to Dr. D. Pines for drawing our attention to (A-10) and this argument.

Table I. Atomic radii (in Å) in metals and oxides.

| | Be | Mg | Zn | Cd | Hg |
|---|---|---|---|---|---|
| M-O | 2.10 | 2.59 | 2.35 | 2.52 | 2.53 |
| $R_{ox}$ | 1.27 | 1.76 | 1.52 | 1.69 | 1.70 |
| $R_m$ | 1.24 | 1.76 | 1.53 | 1.72 | 1.77 |

Table II. Elastic shear constants of aluminum in $10^{11}$ dyne $cm^{-2}$.

| | Total[a] Obs. | Ewald[b] | Band[c] Struct. |
|---|---|---|---|
| $C_{44}$ | ~~1.5~~ 2.5 | 17.2 | ~~-15.7~~ |
| $\frac{1}{2}(C_{11}-C_{12})$ | ~~3.4~~ 2.5 | 1.9 | 1.5 0.6 |

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[b] Reference 7, p. 149.

[c] By difference.

Table III. Distortion of indium.

| | Obs. | Calc. AH | Calc. CB |
|---|---|---|---|
| $\frac{1}{2}(C_{11}-C_{12})$ | $-0.1^{a}$ | -1.9 | $\approx 0.2^{b}$ |
| c/a | 1.08 | 1.25 | -- |

Note: The first line gives the elastic constant in units of $10^{11}$ dyne $cm^{-2}$ for the hypothetical f c c structure and the second line the equilibrium value of c/a.

[a] Extrapolated from the data of Reference 31.

[b] Contributions from $g < 2k_F$ only.

FIGURE CAPTIONS

Fig. 1. The function f(q) in units of $\Omega k_F/4\pi^2$.

Fig. 2. Model potential of indium (in Ry). Also indicated are pseudopotential parameters deduced from the optical spectrum of InSb (reference 26).

Fig. 3. The energy-wave number characteristic $E(q) = v^2F$ (schematic).

Fig. 4. Zeros $q_o$ for divalent and trivalent metals compared with $2k_F$, and the structural weights W(g) for f c c, h c p (ideal c/a) and b c c structures. Units for q and g are $2\pi/A_o$.

Fig. 5. Contribution to $\frac{1}{2}(C_{11}-C_{12})$ from reciprocal lattice vectors less than $2k_F$, as a function of $q_o$, for the pseudopotential of Eq. (13), using the atomic volume of indium. Units are $10^{11}$ dyne $cm^{-2}$.

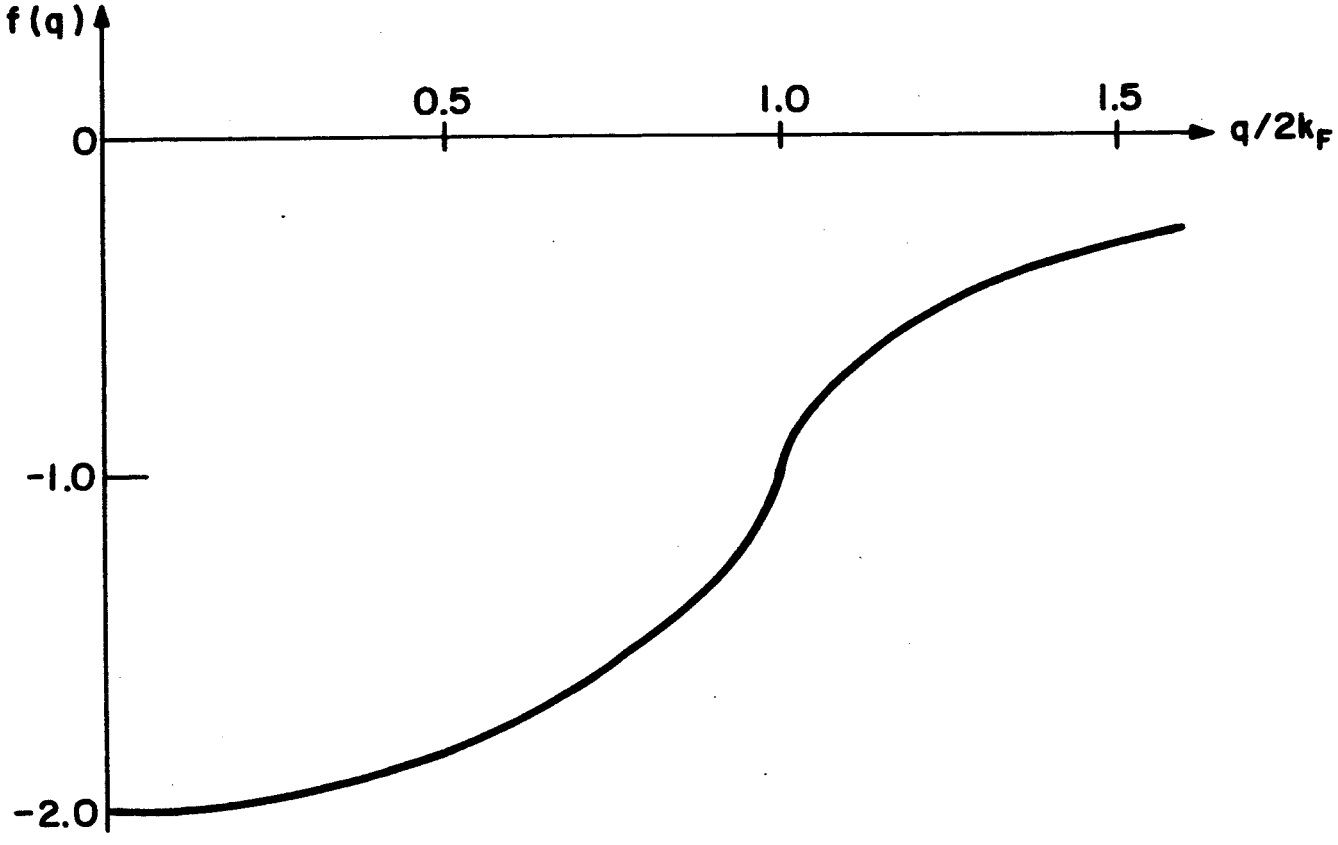


Fig. 1

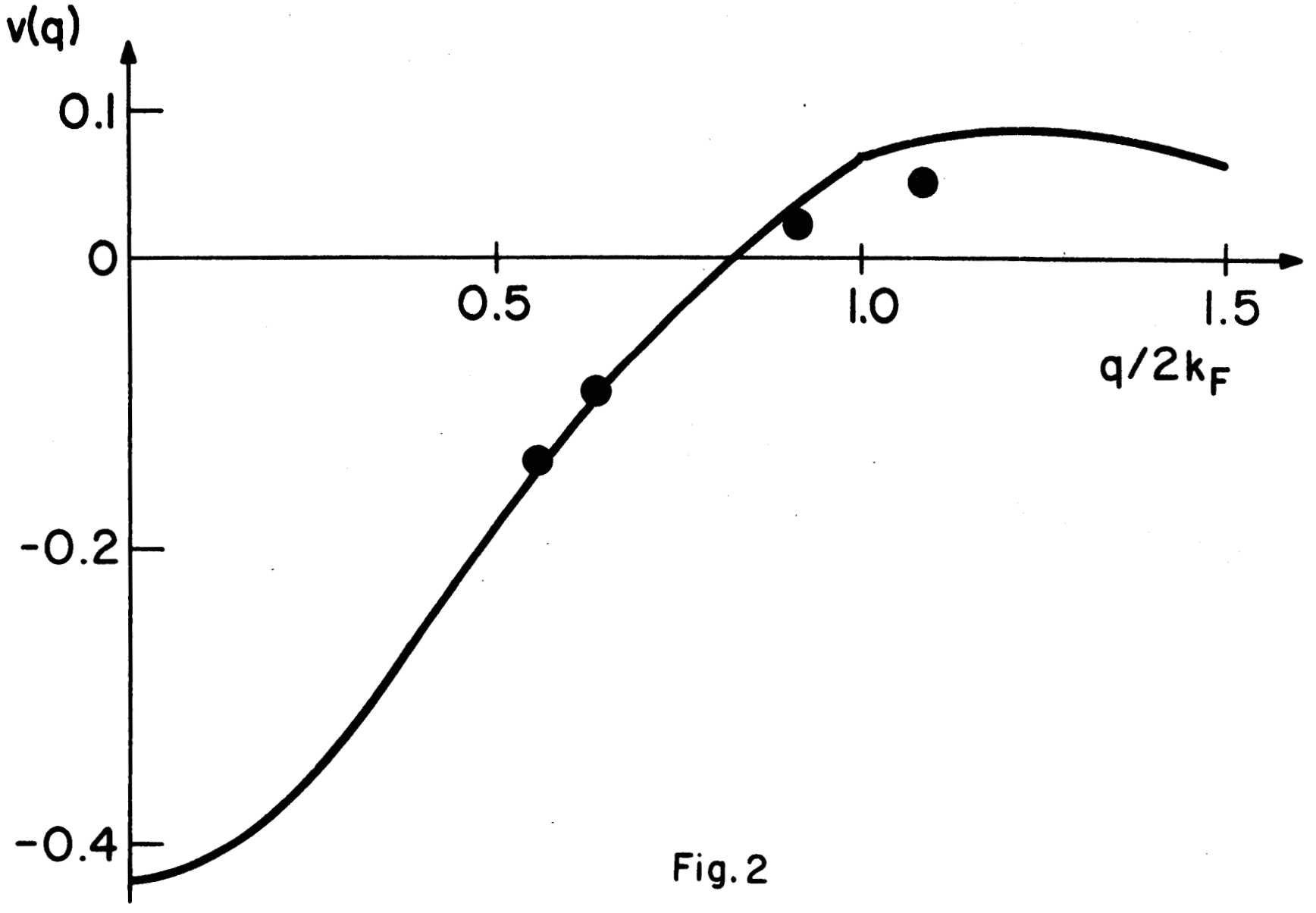


Fig. 2

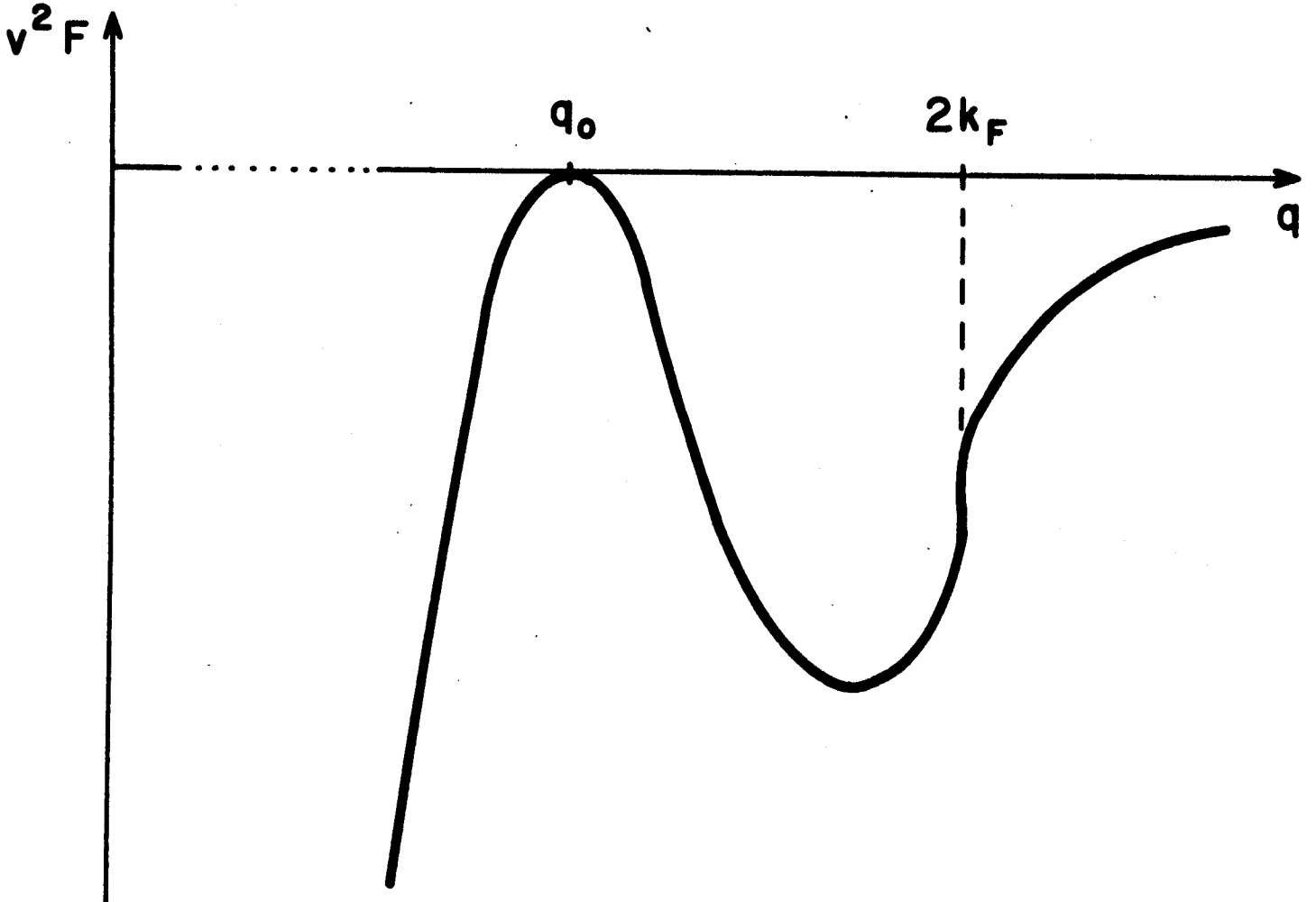


Fig. 3

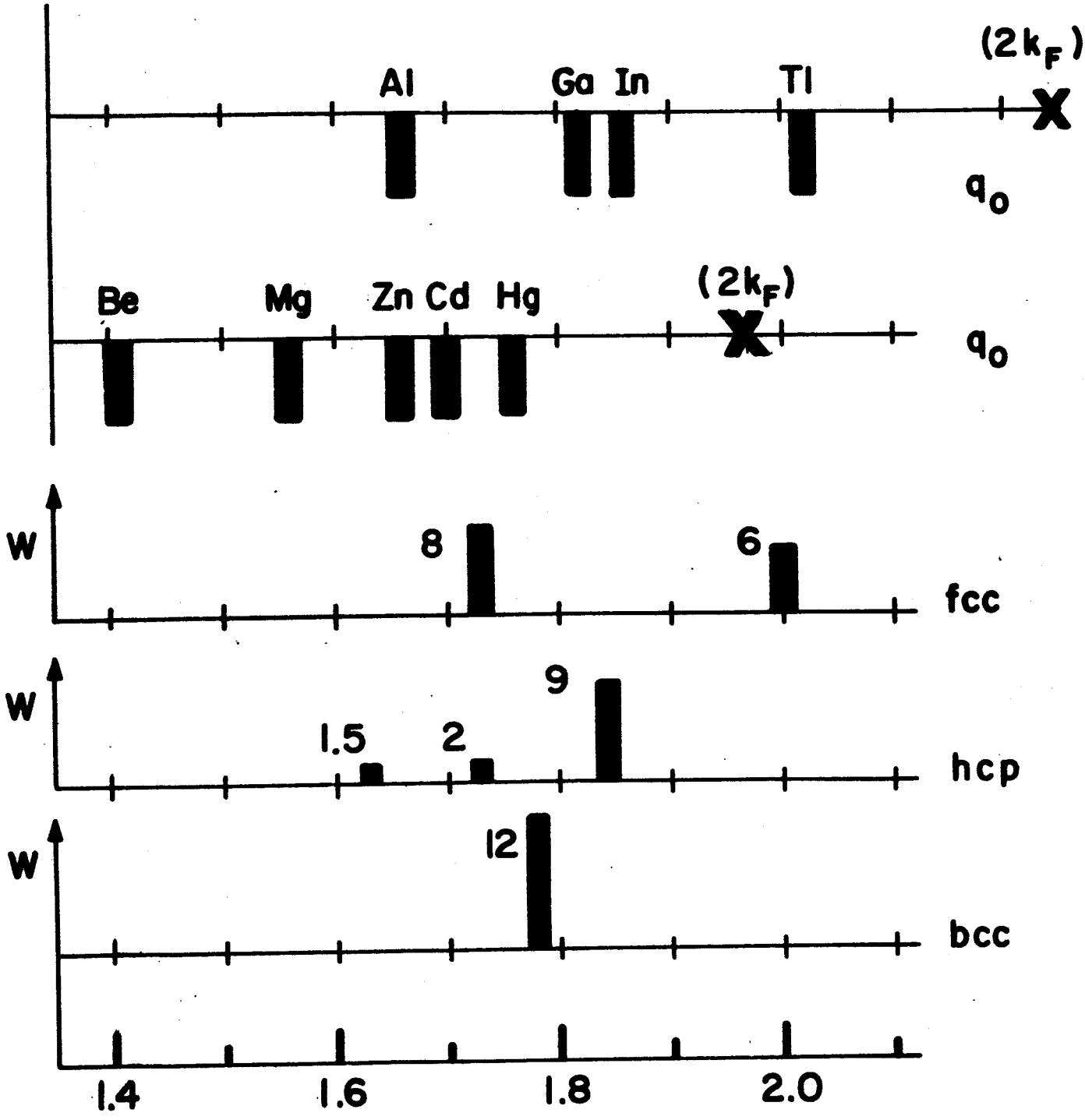
(2k_F)
Al
Ga In
Tl
q_o
Be
Mg
Zn Cd Hg
(2k_F)
q_o
W
8
6
fcc
W
9
1.5
2
hcp
W
12
bcc
1.4
1.6
1.8
2.0

Fig. 4

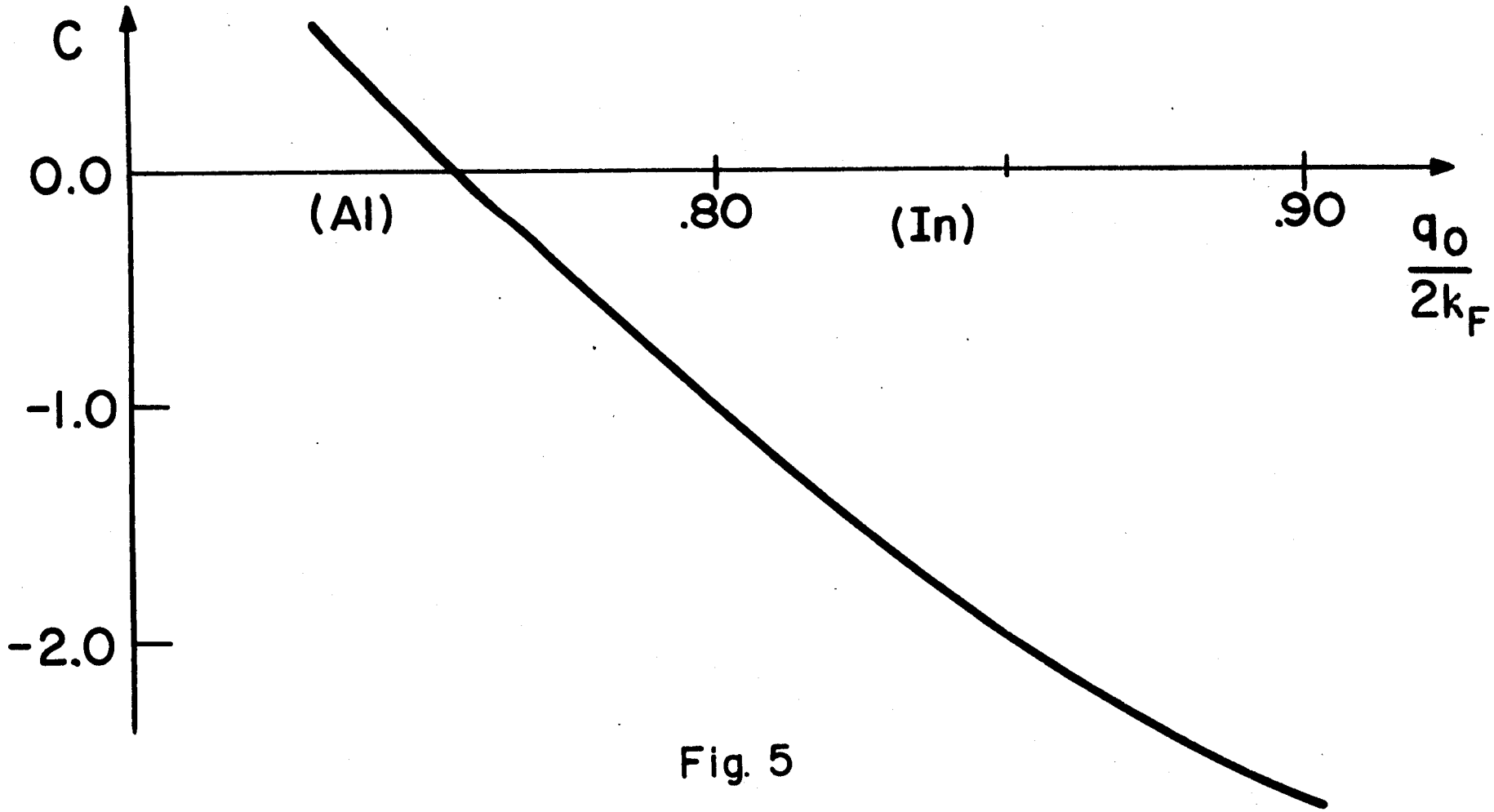


Fig. 5